

## CLAIMS

**What is claimed is:**

1. A method of coupling an organic molecule to a surface of a Group IV element, said method comprising:

5 halogenating said group IV element surface;  
 providing a solution comprising said organic molecule wherein said organic molecule is alcohol terminated and said alcohol-terminated organic molecule is in solvent; and

contacting said solution with said surface under conditions where said solvent is rapidly removed from said surface whereby said organic molecule is coupled to said surface through an E-O bond where E is said group IV element.

2. The method of claim 1, wherein said Group IV element is silicon or germanium.

3. The method of claim 2, wherein said surface is a doped germanium surface.

4. The method of claim 2, wherein said surface is a doped silicon surface.

5. The method of claim 4, wherein said surface is an n-doped silicon surface.

6. The method of claim 4, wherein said surface is a p-doped silicon surface.

7. The method of claim 2, wherein said surface is a hydrogen passivated surface.

8. The method of claim 2, wherein said contacting is in the presence of a base.

9. The method of claim 2, wherein said contacting is in the presence of a base selected from the group consisting of 2,4,6-collidine, 2,6-lutidine, 2,6-di-*tert*-butylpyridine, 4-dimethylaminopyridine, trimethylamine, triethylamine, tributylamine, *N,N*-diisopropylethylamine, 1,8-bis(dimethylamino)naphthalene, 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, Na<sub>2</sub>CO<sub>3</sub>, and NH<sub>3</sub>.

10. The method of claim 2, wherein said organic molecule is a redox-active molecule.

11. The method of claim 10, wherein said organic molecule is selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, and a peri-bridged naphthalene dichalcogenide.

12. The method of claim 10, wherein said organic molecule comprises a molecule selected from the group consisting of a porphyrin, an expanded porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrinic sandwich coordination complex, and a porphyrin array.

13. The method of claim 10, wherein said organic molecule comprises a porphyrinic macrocycle substituted at a  $\beta$ - position or at a *meso*- position.

14. The method of claim 10, wherein said organic molecule comprises a porphyrinic macrocycle containing at least two porphyrins of equal energies held apart from each other at a spacing less than about 50 Å such that said molecule has an odd hole oxidation state permitting the hole to hop between said two porphyrins and wherein said odd hole oxidation state is different from and distinguishable from another oxidation state of said porphyrinic macrocycle.

15. The method of claim 2, wherein said contacting comprises selectively applying said solution to certain regions of said group IV element surface and not to other regions.

16. The method of claim 15, wherein said contacting comprises:  
 placing a protective coating on said surface in regions where said  
 organic molecule is not to be attached;  
 contacting said solution with the surface; and removing the protective  
 5 coating to provide regions of the surface without said organic molecule.

17. The method of claim 15, wherein said contacting comprises contact  
 printing said solution onto said surface.

18. The method of claim 15, wherein said contacting comprises inkjet  
 printing said solution onto said surface.

10 19. The method of claim 15, wherein said contacting comprises spraying  
 or dropping said solution onto said surface.

20. The method of claim 2, wherein said contacting comprises coating  
 said surface with said solution.

15 21. The method of claim 20, wherein said method further comprises  
 etching regions of said surface to remove said organic molecule.

22. The method of claim 2, wherein the alcohol terminated organic  
 molecule is terminated with an alcohol selected from the group consisting of a primary  
 alcohol, a secondary alcohol, a tertiary alcohol, a benzyl alcohol, and an aryl alcohol.

20 23. The method of claim 2, wherein said solvent is a high-boiling  
 solvent.

24. The method of claim 23, wherein said solvent is selected from the  
 group consisting of mesitylene, durene, *o*-dichlorobenzene, 1,2,4,-trichlorobenzene, 1-  
 chloronaphthalene, 2-chloronaphthalene, *N,N*-dimethylformamide, *N,N*-dimethylacetamide,  
*N,N*-dimethylpropionamide, benzonitrile, and anisole.

25 25. The method of claim 23, wherein said surface is heated and said  
 solution is applied to said surface whereby said solvent boils off of said surface.

26. The method of claim 25, wherein said surface is heated to a temperature of at least about 70°C.

27. The method of claim 2, wherein said solvent is applied to said surface and said surface is subjected to a vacuum that boils said solvent off of said surface.

28. The method of claim 2, wherein said halogenating comprises contacting said surface with a halogen selected from the group consisting of iodine, bromine, fluorine, and chlorine.

29. The method of claim 28, wherein said halogenating comprises contacting said surface with iodine.

30. The method of claim 28, wherein said halogenating comprises contacting said surface with a reagent selected from the group consisting of *N*-bromosuccinimide, *N*-chlorosuccinimide, *N*-iodosuccinimide, ICl, SO<sub>2</sub>Cl<sub>2</sub>, BrCCl<sub>3</sub>, PCl<sub>5</sub>, CBr<sub>4</sub>, Br<sub>2</sub> + HgO, MoCl<sub>5</sub>, CF<sub>3</sub>OF, AgSbF<sub>6</sub>, PhSe(O)Cl, AlCl<sub>3</sub>, AlBr<sub>3</sub>, and Cl<sub>2</sub>O.

31. The method of claim 28, wherein said halogenating comprises contacting said surface with a free radical initiator.

32. The method of claim 31, wherein said halogenating comprises contacting said surface with a free radical initiator selected from the group consisting of UV light, benzoyl peroxide, and AIBN (2,2'-azobisisobutyronitrile).

33. A silicon surface having an organic molecule coupled thereto through an Si-O bond wherein said organic molecule is coupled to said surface by the method of claim 2.

34. A germanium surface having an organic molecule coupled thereto through an Ge-O bond wherein said organic molecule is coupled to said surface by the method of claim 2.

35. The surface of any one of claims 33 or 34, wherein said surface is doped.

36. The surface of any one of claims 33 or 34, wherein said organic molecule is a redox-active molecule.

37. The surface of claim 36, wherein said surface can retain a charge per unit area of at least about  $100 \mu \text{ coulombs per cm}^2$  for each non-zero oxidation state of said redox-active molecule.

38. A method of coupling an organic molecule to a surface of a Group IV element, said method comprising:

halogenating said surface;

providing a solution comprising said organic molecule wherein said organic molecule is thiol-terminated and said thiol-terminated organic molecule is in solvent; and

contacting said solution with said surface under conditions where said solvent is rapidly removed from said surface whereby said organic molecule is coupled to said surface through an E-S- bond where E is said group IV element.

39. The method of claim 38, wherein said Group IV element is silicon or germanium.

40. The method of claim 39, wherein said surface is a doped germanium surface.

41. The method of claim 39, wherein said surface is a doped silicon surface.

42. The method of claim 41, wherein said surface is an n-doped silicon surface.

43. The method of claim 41, wherein said surface is a p-doped silicon surface.

44. The method of claim 39, wherein said surface is a hydrogen passivated surface.

45. The method of claim 39, wherein said contacting is in the presence of a base.

46. The method of claim 39, wherein said contacting is in the presence of a base selected from the group consisting of 2,4,6-collidine, 2,6-lutidine, 2,6-di-*tert*-butylpyridine, 4-dimethylaminopyridine, trimethylamine, triethylamine, tributylamine, *N,N*-diisopropylethylamine, 1,8-bis(dimethylamino)naphthalene, 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, Na<sub>2</sub>CO<sub>3</sub>, and NH<sub>3</sub>.

47. The method of claim 39, wherein said organic molecule is a redox active molecule.

48. The method of claim 47, wherein said organic molecule is selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, a and a peri-bridged naphthalene dichalcogenide.

49. The method of claim 47, wherein said organic molecule comprises a molecule selected from the group consisting of a porphyrin, an expanded porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrin sandwich coordination complex, porphyrinic sandwich coordination complex, and a porphyrin array.

50. The method of claim 47, wherein said organic molecule comprises a porphyrinic macrocycle substituted at a  $\beta$ - position or at a *meso*- position.

51. The method of claim 47, wherein said organic molecule comprises a porphyrinic macrocycle containing at least two porphyrins of equal energies held apart from each other at a spacing less than about 50 Å such that said molecule has an odd hole oxidation state permitting the hole to hop between said two porphyrins and wherein said odd hole oxidation state is different from and distinguishable from another oxidation state of said porphyrinic macrocycle.

52. The method of claim 39, wherein said contacting comprises selectively applying said solution to certain regions of said silicon surface and not to other regions.

53. The method of claim 52, wherein said contacting comprises:  
 5 placing a protective coating on said surface in regions where said organic molecule is not to be attached;  
 contacting said solution with said silicon surface; and removing the protective coating provide regions of the silicon surface without said organic molecule.

54. The method of claim 52, wherein said contacting comprises contact  
 10 printing said solution onto said surface.

55. The method of claim 52, wherein said contacting comprises inkjet  
 printing said solution onto said surface.

56. The method of claim 52, wherein said contacting comprises spraying  
 or dropping said solution onto said surface.

57. The method of claim 39, wherein said contacting comprises coating  
 15 said surface with said solution.

58. The method of claim 57, wherein said method further comprises  
 etching regions of said surface to remove said organic molecule.

59. The method of claim 39, wherein the thiol- terminated organic  
 20 molecule is terminated with a thiol selected from the group consisting of a primary thiol, a secondary thiol, a tertiary thiol, a benzyl thiol, and an arylthiol.

60. The method of claim 39, wherein said solvent is a high-boiling  
 solvent.

61. The method of claim 60, wherein said solvent is selected from the  
 25 group consisting of mesitylene, durene, *o*-dichlorobenzene, 1,2,4,-trichlorobenzene, 1-chloronaphthalene, 2-chloronaphthalene, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N,N*-dimethylpropionamide, benzonitrile, and anisole.

62. The method of claim 60, wherein said surface is heated and said solution is applied to said surface whereby said solvent boils off of said surface.

63. The method of claim 60, wherein said surface is heated to a temperature of at least about 70°C.

64. The method of claim 39, wherein said solvent is applied to said surface and said surface is subjected to a vacuum that boils said solvent off of said surface.

65. The method of claim 39, wherein said halogenating comprises contacting said surface with a halogen selected from the group consisting of iodine, bromine, fluorine, and chlorine.

66. The method of claim 28, wherein said halogenating comprises contacting said surface with iodine.

67. The method of claim 28, wherein said halogenating comprises contacting said surface with a reagent selected from the group consisting of *N*-bromosuccinimide, *N*-chlorosuccinimide, *N*-iodosuccinimide, ICl, SO<sub>2</sub>Cl<sub>2</sub>, BrCCl<sub>3</sub>, PCl<sub>5</sub>, CBr<sub>4</sub>, Br<sub>2</sub> + HgO, MoCl<sub>5</sub>, CF<sub>3</sub>OF, AgSbF<sub>6</sub>, PhSe(O)Cl, AlCl<sub>3</sub>, AlBr<sub>3</sub>, and Cl<sub>2</sub>O.

68. The method of claim 39, wherein said halogenating comprises contacting said surface with a free radical initiator.

69. The method of claim 39, wherein said halogenating comprises contacting said surface with a free radical initiator selected from the group consisting of UV light, benzoyl peroxide, and AIBN (2,2'-azobisisobutyronitrile).

70. A redox-active substrate comprising a silicon or germanium surface having attached thereto a redox-active molecule where:  
 when said surface is silicon, said redox-active molecule is attached to said silicon surface through an Si-O bond or an Si-S bond;  
 when said surface is germanium, said redox-active molecule is attached to said silicon surface through a Ge-O bond or a Ge-S bond;



and said redox-active substrate can retain a charge per unit area of at least about 100  $\mu$  coulombs per  $\text{cm}^2$  for each non-zero oxidation state of said redox-active molecule.

71. The substrate of claim 70, wherein said silicon surface is a doped  
5 silicon surface.

72. The substrate of claim 71, wherein said surface is an n-doped silicon surface.

73. The substrate of claim 71, wherein said surface is a p-doped silicon surface.

10 74. The substrate of claim 70, wherein said silicon surface is a doped germanium surface.

75. The substrate of claim 71, wherein said surface is an n-doped germanium surface.

15 76. The substrate of claim 71, wherein said surface is a p-doped germanium surface.

77. The substrate of claim 70, wherein said surface is a hydrogen passivated surface.

20 78. The substrate of claim 70, wherein said redox-active molecule is selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, and a peri-bridged naphthalene dichalcogenide.

25 79. The substrate of claim 70, wherein said redox-active molecule comprises a molecule selected from the group consisting of a porphyrin, an expanded

porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a sandwich coordination complex, and a porphyrin array.

80. The substrate of claim 70, wherein said redox-active molecule comprises a porphyrinic macrocycle substituted at a  $\beta$ - position or at a *meso*- position.

81. The substrate of claim 70, wherein said substrate further comprises integrated circuit elements.

82. The substrate of claim 81, wherein said circuit elements are selected from the group consisting of a transistor, a diode, a logic gate, and a rectifier.

83. An apparatus for storing data, said apparatus comprising:  
a fixed electrode electrically coupled to  
a redox active molecule having two or more different and  
distinguishable oxidation states wherein data is stored in said oxidation states by the  
addition or withdrawal of one or more electrons from said storage medium via the  
electrically coupled electrode, and further wherein  
said redox-active molecule is coupled to a silicon surface through an  
Si-O bond or said redox-active molecule is coupled to a germanium surface through a Ge-  
O- bond.

84. The apparatus of claim 83, wherein said apparatus can retain a charge per unit area of at least about  $100 \mu\text{Coulombs per cm}^2$  for each non-zero oxidation state of said redox-active molecule.

85. The apparatus of claim 83, wherein said apparatus stores data at a density of at least one bit per molecule.

86. The apparatus of claim 83, wherein said redox-active molecule has at least eight different and distinguishable oxidation states.

87. The apparatus of claim 83, wherein said redox-active molecule is electronically coupled to a second fixed electrode that is a reference electrode.

88. The apparatus of claim 83, wherein said redox-active molecule is present at a multiplicity of locations on said silicon surface.

89. The apparatus of claim 88, wherein each location is addressed by a single electrode.

90. The apparatus of claim 88, wherein each location is addressed by two electrodes.

91. The apparatus of claim 83, wherein said electrode is connected to a voltage source.

92. The apparatus of claim 91, wherein said voltage source is the output of an integrated circuit.

93. The apparatus of claim 83, wherein said electrode is connected to a device to read the oxidation state of said redox-active molecule.

94. The apparatus of claim 83, wherein said redox-active molecule is selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, and a peri-bridged naphthalene dichalcogenide.

95. The apparatus of claim 83, wherein said redox active molecule is selected from the group consisting of a porphyrin, an expanded porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrinic sandwich coordination complex, and a porphyrin array.

96. The apparatus of claim 83, wherein said redox-active molecule comprises a porphyrinic macrocycle substituted at a  $\beta$ - position or at a meso- position.

97. A method of fabricating an ordered molecular assembly, said method comprising:

halogenating a silicon surface;

providing a solution comprising an organic molecule wherein said organic molecule is alcohol- or thiol- terminated and said alcohol- or thiol-terminated organic molecule is in solvent; and

5 contacting said solution with said silicon surface at a multiplicity of discrete locations on said surface under conditions where said solvent is rapidly removed from said surface whereby said organic molecule is coupled to said surface through an Si-O or an Si-S- bond.

98. A method of fabricating an ordered molecular assembly, said method

10 comprising:

halogenating a germanium surface;

providing a solution comprising an organic molecule wherein said organic molecule is alcohol- or thiol- terminated and said alcohol- or thiol-terminated organic molecule is in solvent; and

15 contacting said solution with said silicon surface at a multiplicity of discrete locations on said surface under conditions where said solvent is rapidly removed from said surface whereby said organic molecule is coupled to said surface through an Ge-O or an Ge-S- bond.

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